U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-262 234

Evaluation of a Prototype Instrument for Determining Phosphorus in Water

Environmental Research Lab, Athens, Ga

Oct 76

PB 262 234

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/4-76-033		

4. TITLE AND SUBTITLE	5. REPORT DATE
EVALUATION OF A PROTOTYPE INSTRUMENT FOR DETERMINING PHOSPHORUS IN WATER	October 1976 (Issuing Date)
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Thomas B. Hoover J. MacArthur Long	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Athens, Georgia 30601	1BA027; ROAP 16ADN, Task 72
	11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Same as above	Final
	14. SPONSORING AGENCY CODE EPA-ORD

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A second-generation flame spectrometer for the direct determination of phosphorus in water was evaluated. Response to phosphorus in the form of phosphoric acid was linear from 0.5 to 16 ppm phosphorus. The relative standard deviation was approximately constant at 20 percent over the range.

River water and municipal sewage effluent were analyzed after the addition of phosphoric acid (1.8 ppm P) and filtration through a series of microporous membranes. Recovery of the added phosphorus averaged 70 percent for the river water and 95 percent for the sewage effluent after treatment with cation exchange resin. There was no clear relation to filter pore size in the range 5 to 0.2 micrometers. Analyses of the higher range EPA Nutrient Reference Samples (approximately 0.5 ppm P) agreed within one standard deviation with the reference values, both for inorganic and total phosphorus. The lower concentration range samples (approximately 0.1 ppm P) gave barely detectable signals.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Phosphorus, *Spectrometers, *Flame Photometry, *Emission, *Inorganic Compounds	Flame Emission	07B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to Public	UNCLASSIFIED	25
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	3.50-3.00

EPA Form 2220-1 (9-73)

☆ U.S. GOVERNMENT PRINTING OFFICE: 1976-757-056/5423 Region No. 5-11

EPA-600/4-76-033
October 1976

EVALUATION OF A PROTOTYPE INSTRUMENT FOR DETERMINING PHOSPHORUS IN WATER

by

Thomas B. Hoover
J. MacArthur Long
Environmental Research Laboratory
Athens, Georgia 30601

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ATHENS, GEORGIA 30601

ia

DISCLAIMER

This report has been reviewed by the Athens Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

A second-generation flame spectrometer for the direct determination of phosphorus in water was evaluated. Response to phosphorus in the form of phosphoric acid was linear from 0.5 to 16 ppm phosphorus. The relative standard deviation was approximately constant at 20 percent over the range.

River water and municipal sewage effluent were analyzed after the addition of phosphoric acid (1.8 ppm P) and filtration through a series of microporous membranes. Recovery of the added phosphorus averaged 70 percent for the river water and 95 percent for the sewage effluent after treatment with cation exchange resin. There was no clear relation to filter pore size in the range 5 to 0.2 micrometers. Analyses of the higher range EPA Nutrient Reference Samples (approximately 0.5 ppm P) agreed within one standard deviation with the reference values, both for inorganic and total phosphorus. The lower concentration range samples (approximately 0.1 ppm P) gave barely detectable signals.

Suggestions are given for further development of the instrument.

This report was submitted in fulfillment of ROAP 16ADN, Task 72 by the Environmental Research Laboratory, Athens, Georgia, under the sponsorship of the Environmental Protection Agency. Work was completed as of October 1975.

CONTENTS

Sections		Page
I	Conclusions	1
II	Recommendations	2
III	Introduction	3
IV	Experimental	4
V	Discussion	16
VI	References	18

Preceding page blank

FIGURES

No.		Page
1.	Background Response as a Function of Air/Hydrogen Ratios	6
2.	Response to 1.8 ppm P (As Phosphoric Acid) as a Function of Air Inlet Rate	7
3.	Characteristic Response to Phosphoric Acid	9
4.	Calibration Curve for Phosphoric Acid	10
5.	Effect of Adding Cations	12

TABLES

No.		Page
1.	Analyses of Natural and Waste Water Filtered Through Microporous Membranes.	14
2.	Analysis of EPA Nutrient Reference Samples.	15

SECTION I

CONCLUSIONS

Dissolved phosphorus in water, in either organic or inorganic forms, was determined in the range 0.5 to 16 milligrams phosphorus per liter.

The relative standard deviation of a determination was about 20% over the entire analytical range.

No particle size effects, in the range 0.2 to 5 micrometers, were detectable either in river water or in municipal sewage effluent.

The instrument requires considerably more modification to achieve convenient, safe, and reliable operation.

SECTION II

RECOMMENDATIONS

The following mechanical modifications should be made:

- installation of a fail-safe flame indicator to shut off hydrogen flow when the burner goes out,
- positive disposal of excess hydrogen from the vent,
- more direct introduction of the water sample,
- easily changeable photoemission tube, and
- output signal logarithmically related to the emission intensity.

Because of problems inherent in the "cool-flame" emission method, it is not certain that the instrument can be made to respond to total phosphorus in water at environmentally significant concentrations (0.01 to 1.0 mg P/l).

SECTION III

INTRODUCTION

Eutrophication of fresh water lakes and streams deteriorates the quality of the environment and has been ascribed to increased inputs of plant nutrients through human activities. Phosphorus seems most often to be a critical nutrient in this process and can be controlled in the treatment of municipal wastes. Consequently, there is increased emphasis on phosphorus removal in waste treatment and a greater need for a rapid, simple, analytical method for monitoring phosphorus concentrations during such processes.

This report evaluates a second-generation prototype instrument for determining phosphorus in water samples by flame photometry. The phosphorus hydride oxide radical (HPO) is formed and excited in a cool, hydrogen-rich flame. The chemiluminescent decay of the radical emits green light at 525 nm, which is isolated by an interference filter and measured by a phototube. Construction (1) and evaluation (2) of the original prototype have been reported.

The present instrument was very similar in principle of operation to the original model (3). The entire sample system (sample inlet, burner, emission tube) was operated below ambient pressure by an aspirator driven by a compressed air supply. This feature prevented the inadvertent escape of hydrogen through leaks, although the final exhaust, containing unburned hydrogen, was vented to the room.

A major modification was provision for passing the entire nebulized sample through the burner. Previously, a large excess of aerosol was directed at the face of the instrument, a portion being drawn into the burner by the reduced pressure created by the aspirator. That procedure was considered unacceptable for use with pathogen-containing water specimens because of the health risk to the operator from the excess aerosol discharged to the room.. In the present model a separately controlled air stream passed through the ultrasonic nebulizer containing the sample and the resulting aerosol was directed into the burner inlet, together with some additional room air.

The optical and electronic components were modified to provide greater freedom from light leaks and to improve the stability of the amplifier output.

SECTION IV

EXPERIMENTAL

MODIFICATIONS OF INSTRUMENT

Several changes in the flow controls were made immediately. As supplied, the instrument had a micrometer-scaled needle valve control, but no flow meter, in the air line driving the aspirator; a branch line from the air compressor supplied cooling air to the phototube housing and contained a flowmeter with a control valve at the inlet. The hydrogen fuel flow was also controlled by the inlet valve of its flowmeter. The manufacturer's recommendation for setting flow rates included setting the needle-valve fully open and adjusting the aspirator air indirectly through control of the cooling air.

Since hydrogen flow rate is one of the most critical factors in the burner operation, the needle valve was moved to the hydrogen line and a flow meter was placed in the aspirator line for direct measurement and control. All flow meters had scale calibrations in standard liters (or cubic centimeters) of air per minute and were not recalibrated or corrected. Consequently, the actual flow rates of hydrogen were considerably greater than the nominal "air" values. The flow rate for a given meter reading is approximately inversely proportional to the density of the fluid (4). Consequently, hydrogen flow rates were approximately four times the rate indicated for air. Meter readings were used as relative measures for empirical adjustment of the burner operation.

Optimum burner design is critical to the success of the instrument and was a major consideration in the original contract (1). Since the detection limit of the second generation prototype was poorer than that of the original, some additional investigations were made. Conflicting requirements must be compromised: a high flame temperature favors evaporation of the aerosol droplets and decomposition of the phosphorus compounds, while a low temperature (5,6) and excess hydrogen are necessary to excite the chemiluminescence. Among the modifications tried were:

- sample introduction to an air-rich flame, with secondary hydrogen admitted just above the orifice.
- axial introduction of the aerosol, with a surrounding cylindrical jet of hydrogen.

- auxiliary cooling air blowing on the emission tube.

Some qualitative observations were made with a glass Liebig condenser, in which the entire flame could be seen. These suggested that a major function of the orifice is to cool the flame. None of the modifications substantially improved the operation of the burner and it was restored to the manufacturer's configuration, placing the tip of the hydrogen capillary about 5 mm above the burner orifice.

The tip of the orifice tended to become quite hot, especially when the burner was first lighted and operated with excess air. The temperature was sufficient to decompose the silicone rubber gasket sealing the top of the emission tube, resulting in air leaks that quenched the chemiluminescence and in clouding the emission tube with silica. The gasket and emission tube were replaced before further quantitative tests. The inside of the phototube housing was painted flat black to reduce the effect of scattered light, and the passage between the emission tube and aspirator was enlarged to 1/4" I.D. to reduce blockage by condensed moisture (2).

TESTS

Optimization

Burner conditions were optimized by systematically varying hydrogen and inlet air flow rates in order to reduce the background signal when no sample was present, and to maximize the net signal for a fixed phosphorus concentration. Figure 1 shows the background signal for various ratios of inlet air to hydrogen, at two hydrogen flow rates. It will be recalled that the nominal hydrogen flow rates, and the corresponding ratios, are based on meter readings of standard cc of <u>air</u> per minute. The true hydrogen volumetric flow rate is larger by a factor of approximately four, and the ratio is smaller by the same factor. Figure 1 shows a sharp increase in background at a nominal ratio about 1.5. Figure 2 shows the net response to 1.8 ppm P (as phosphoric acid) as a function of inlet air rate. The sample was introduced with a carrier air flow rate of 0.28 l/min, about the maximum for stable flame operation. Figure 2 indicate a broad maximum net response at an inlet air rate of 0.45 l/min and hydrogen rate of 300 cc/min, corresponding to a ratio of 1.5. These conditions were adopted for subsequent tests.

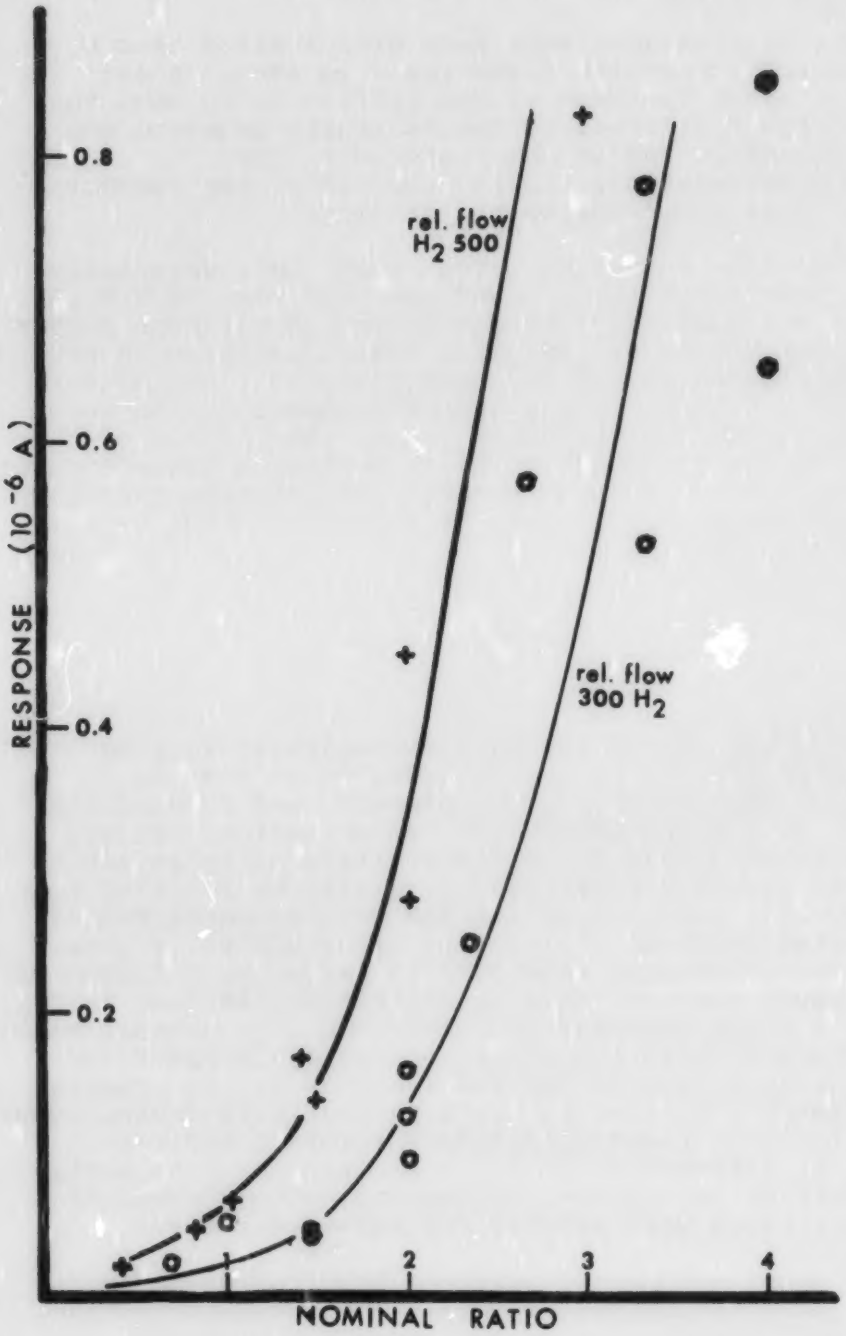

FIGURE 1. Background Response as a Function of Air/Hydrogen Ratios

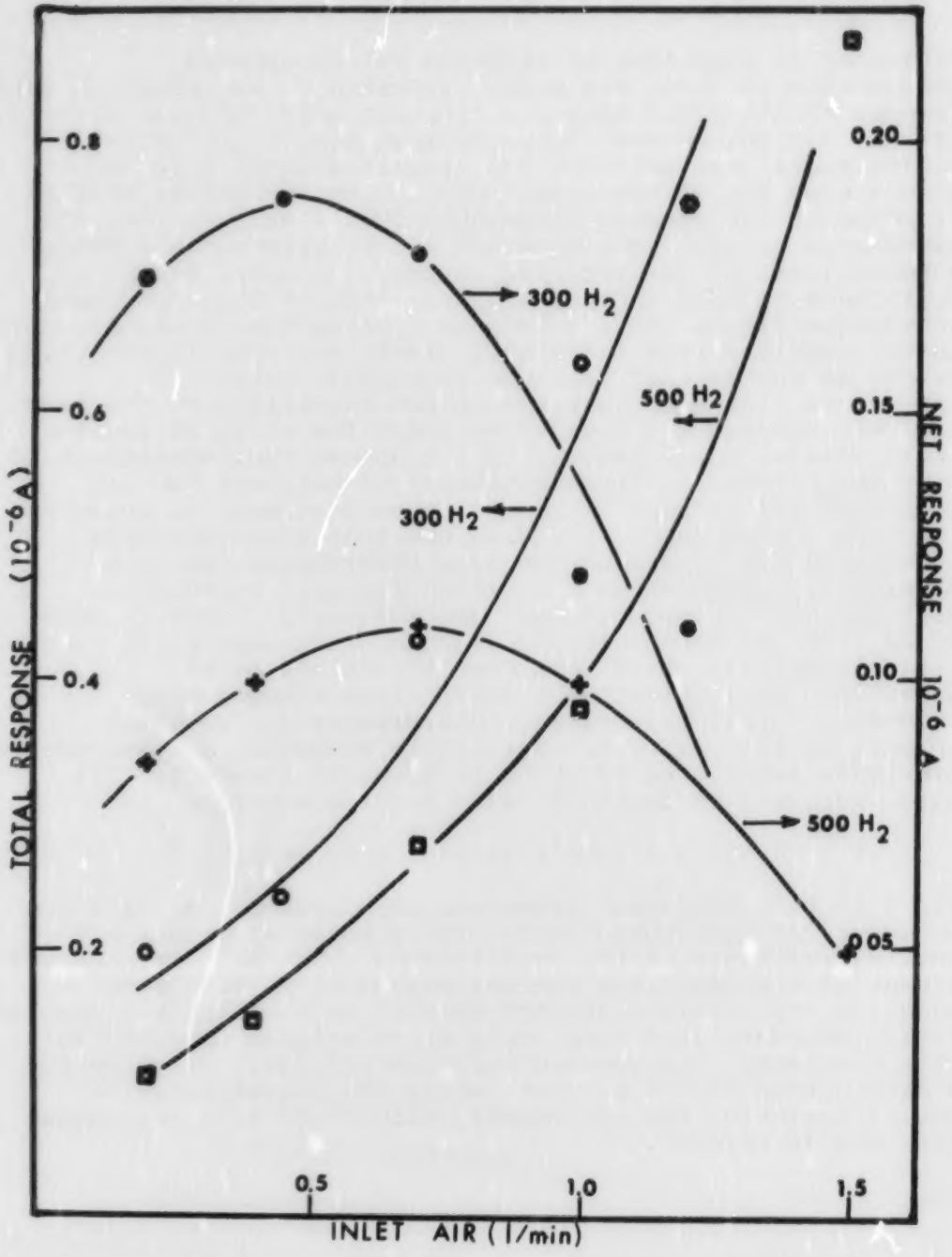

FIGURE 2. Response to 1.8 ppm P (as Phosphoric Acid) as a Function of Inlet Air Rate

Calibration

A series of calibrations of response vs. phosphorus concentration as H_3PO_4 was made. Tracings of the characteristic responses to distilled water, phosphoric acid, and air are shown in Figure 3. In contrast to a previous report (2), a small positive signal was observed for distilled water despite rigorous cleaning of the sample cup, inlet and burner orifice. This response was checked frequently during calibrations and measurements of test solutions and was subtracted as a blank. The noise level of the recorder response to water and H_3PO_4 is clearly much greater in Figure 3 than that of the background air-hydrogen flame. This noise, or fluctuation in signal, which probably resulted from individual liquid droplets in the flame, provided an estimate of variance associated with each measurement. The extreme range of pen excursions on the chart record was squared and divided by twice the width of the record in millimeters, corresponding to a response time equivalent to 0.5 mm chart travel. These estimates of variance for any calibration series were extremely nonhomogeneous, as estimated by the chi-square test. Dividing the individual variance estimates by the square of the mean observation, which is equivalent to postulating a constant relative standard deviation, greatly reduced the nonhomogeneity. (For example, χ^2 reduced from 186 to 66, for 15 degrees of freedom.) In none of three calibrations could more than two-thirds of the observations be considered as coming from a homogeneous population. Nevertheless, each measurement was weighted inversely by its estimated variance in computing a least-squares calibration curve, one of which is shown in Figure 4. The pooled, weighted calibration curve had the equation

$$Y = (0.012 \pm 0.017) + (0.0743 \pm 0.0044)X \qquad (1)$$

where Y is the instrument response, in microamperes, to X ppm phosphorus, as phosphoric acid. The plus-minus values are standard deviations of the coefficients. The calibrations were all made at the same five nominal values of X, with four randomized replications in each series, so that the variance and relative standard deviation could be calculated for each value of the abscissa. The average relative standard deviation for the five points was 20 percent, while the pooled relative standard deviation for all points, calculated from the noise level, was 16 percent.

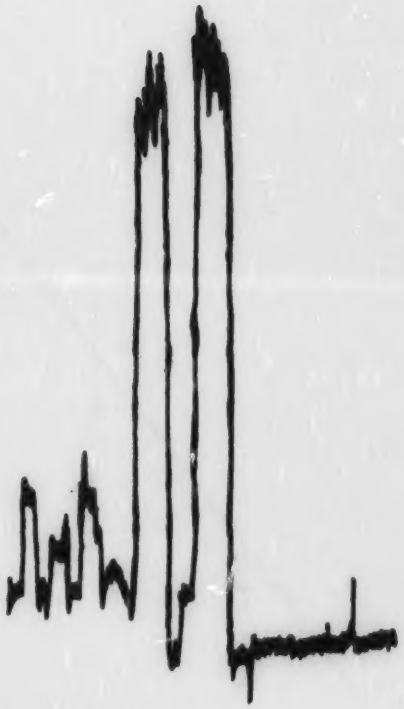

FIGURE 3. Characteristic Response to Phosphoric Acid

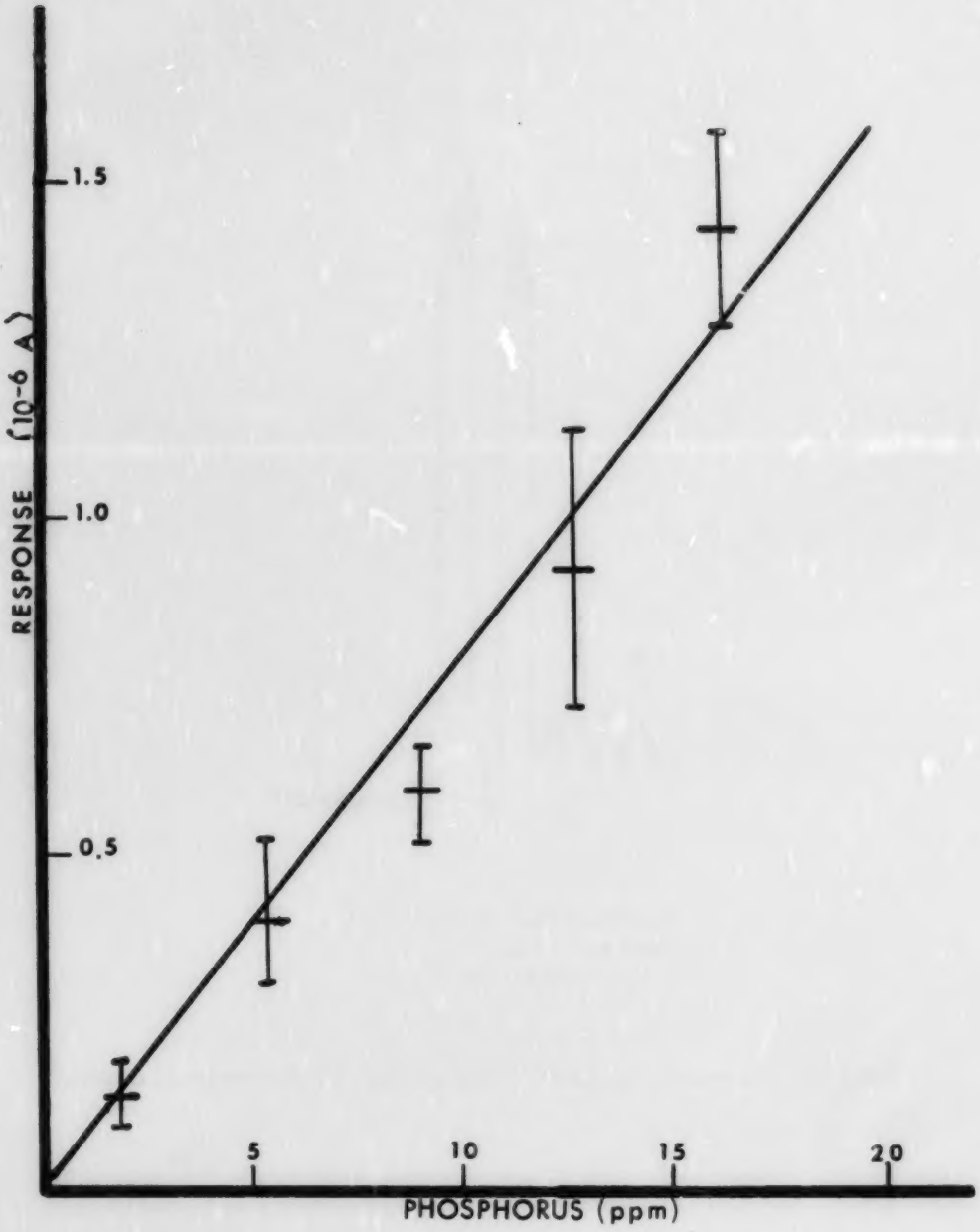

FIGURE 4. Calibration Curve for Phosphoric Acid

Cation Interferences

Additions of potassium, calcium, and magnesium, as the chlorides, were made to solutions of phosphoric acid, containing 9.0 ppm Phosphorus. The results, shown in Figure 5, confirm the findings of Seitz (2) that Ca and Mg markedly inhibited the response to inorganic phosphate. Potassium had an insignificant effect.

Particle Size Effects

The previous inhouse study (2) presented evidence that fine particulate matter in river water reduced the detection of added soluble phosphate by the flame detector. It was inferred that soluble phosphate was closely associated with the particulates and no longer capable of excitation in the low temperature flame. To investigate this matter further, both Oconee River water and effluent from the Athens municipal sewage plant were filtered through a series of microporous filters. At each stage of filtration a water sample was analyzed directly and after addition of a 1.8 ppm spike of phosphoric acid. The analyses were performed both directly and after a batch treatment with Amberlite IR-120 cation exchange resin to remove possible interfering cations. Deionized water blanks were run with each series.

The detailed procedure was the following: the water was filtered through course grade analytical filter paper (S&S No. 588). Two portions of filtrate were taken and one was spiked with 1.8 ppm phosphorus, as phosphoric acid. Each portion was again divided into two portions, one being analyzed directly. The other portions, both of original filtrate and of the spiked sample, were each treated with approximately 1 g ion exchange resin per 10 ml of water by stirring for several minutes. The water was decanted into the sample cup of the analyzer. Most of the filtrate was then filtered through a 5-µm Nuclepore and the filtrate was analyzed as above. The remaining filtrate from the 5-µm filter was passed through a 1-µm Nuclepore, and successively, a 0.45-µm Metricel, and a 0.2-µm Metricel. At each stage four portions of filtrate were analyzed as described. For each analysis, four measurements of instrument response were recorded, with intervening records of the air background signal.

The net response above background was corrected by the corresponding value for deionized water and averaged over the four readings, weighting each by the reciprocal of its variance. The corresponding concentration was determined from the

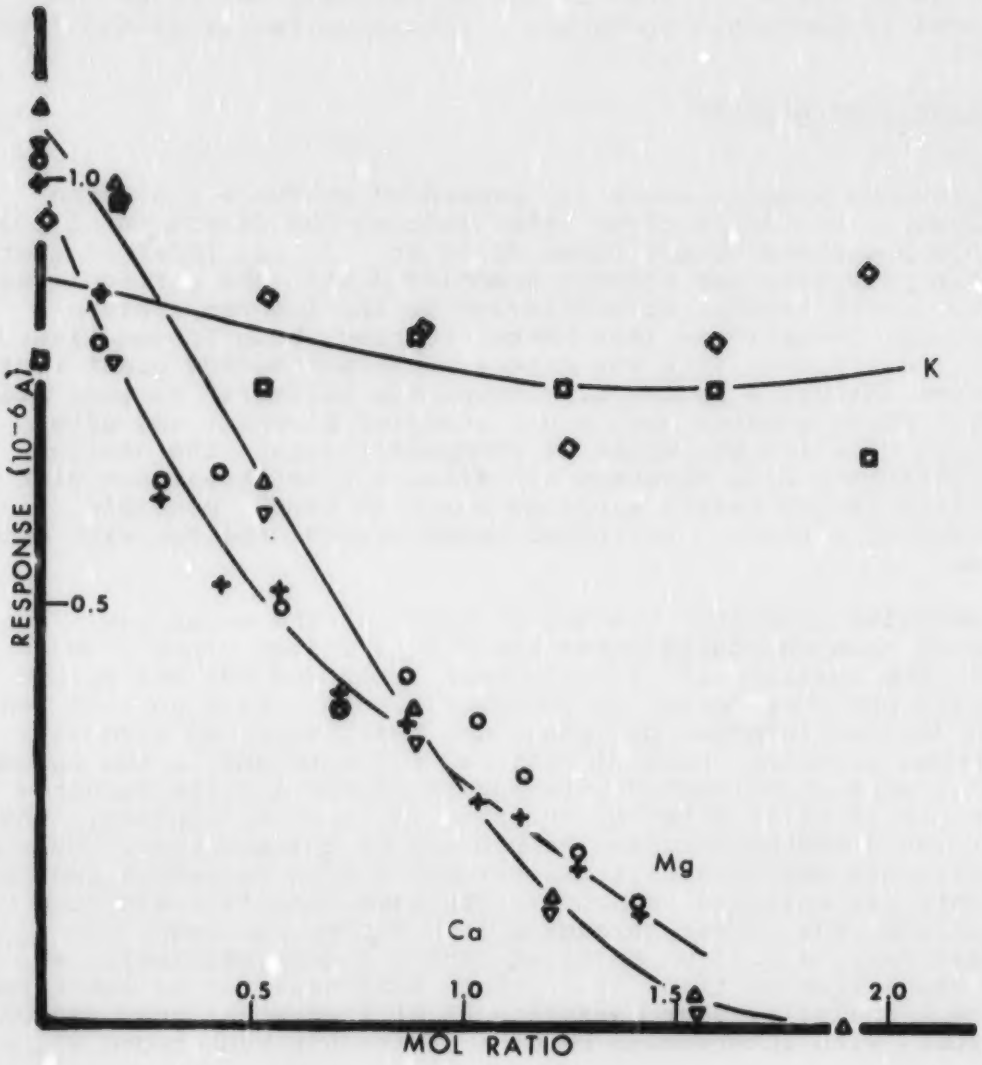

FIGURE 5. Effect of Adding Cations

calibration curve (Equation 1). The fractional recovery of the spike was calculated from

$$R = 2\,C_2/(3.6 + C_1) \qquad (2)$$

where C_1 and C_2 are the concentrations in ppm of the original (unspiked) and spiked sample, respectively. The volume of added spike was equal to the sample volume. Thus, the expected final concentration, for complete recovery, was

$$C_2' = 1.8 + C_1/2 \qquad (3)$$

Results are shown in Table 1. The ± entries represent estimated standard deviations, calculated by propagation-of-error formulas from the variances of the individual chart records. These were estimated as described under Calibration. It will be observed from Table 1 that recoveries from sewage effluent were essentially complete, provided that ion-exchange treatment was used. On the other hand, recoveries were low (about 70 percent) in the river water, regardless of ion-exchange treatment. In neither series was there any clear relation to the pore-size of the filters.

EPA Nutrient Reference Sample

EPA Nutrient Reference Standards were diluted as directed with deionized water and analyzed directly. Also, standard additions of 1.8 ppm P (as phosphoric acid) were made to each solution. No filtration or ion exchange treatment was used. Each analysis is the average of four aspirations with intermediate checks of background, but no replicate solutions were run.

In the fourth and fifth columns of Table 2, concentrations were calculated from the calibration curve and, in column five, corrected for the standard addition. In the sixth column the concentrations were calculated by the method of standard additions, without reference to the calibration curve.

By reference to the nominal values, in the third column of Table 2, it appears that the standard addition method of calibration is more reliable than the use of the calibration curve at these low levels, which are close to the detection limit. The error limits shown in the table were calculated from the noise level of the response, as described previously, and do not seem indicative of the accuracy of the results. There is no significant difference between the inorganic and organic forms of phosphorus.

Table 1. ANALYSES OF NATURAL AND WASTE WATER FILTERED THROUGH MICROPOROUS MEMBRANES

Pore Size (μm)	Filtered C_1	Filtered & Resin-Treated C_1	After Spike (1.8 ppm P) C_2	Resin-treated After Spike C_2	Percent Recovery of Spike (Equation 2) Filtered	Resin-treated
			Oconee River Water			
Coarse	0.76	0.82	1.75	1.85	80 ± 8	84 ± 8
Coarse	0.36	0.37	1.09	1.20	55 ± 9	60 ± 9
5	0.74	0.70	1.54	1.76	71 ± 8	82 ± 10
1	0.74	0.78	1.48	1.49	68 ± 8	68 ± 8
0.45	0.72	0.68	1.64	1.62	76 ± 8	76 ± 8
0.2	0.68	0.73	1.63	1.38	76 ± 8	64 ± 8
0.2	0.27	0.25	1.04	1.37	54 ± 8	71 ± 11
			Municipal Sewage Effluent			
Coarse	2.31	3.43	2.08	3.98	70 ± 8	113 ± 11
5	2.23	3.11	2.10	3.03	72 ± 8	90 ± 8
1	1.93	3.16	1.97	3.00	71 ± 9	89 ± 9
0.45	1.97	3.09	2.04	2.95	73 ± 8	88 ± 9
0.2	2.47	3.30	2.05	3.22	68 ± 8	93 ± 9

Table 2. ANALYSIS OF EPA NUTRIENT REFERENCE SAMPLES

Sample Type	Phosphorus Concentration (ppm) Nominal	Direct Calibration	Spike Calibration	Standard Addition
Inorganic	0.021	0.25 ± 0.07	0.52 ± 0.03	0.014 ± 0.005
Inorganic (Undiluted)	0.393 78.6	0.62 ± 0.08 39.2 ± 2.1	0.21 ± 0.01	0.46 ± 0.04
Organic (Undiluted)	0.142 28.4	0.28 ± 0.07 20.6 ± 1.1	0.59 ± 0.03	0.04 ± 0.03
Organic	0.713	0.76 ± 0.09	0.48 ± 0.02	0.61 ± 0.08

SECTION V

DISCUSSION

This and preceding studies of the flame emission phosphorus analyzer show that it does respond to low levels of organic and inorganic phosphorus in water, but with limitations. The response to inorganic phosphate is strongly inhibited by calcium and magnesium and, presumably, by other cations that form insoluble phosphates. These soluble ions can be removed by ion exchange treatment. River water was shown to contain an interference that was not removed by ion exchange or by filtration through 0.2-μm micropores.

A major drawback of the system appears to be the inability of the low temperature flame to excite all the phosphorus in particulate or insoluble forms. The same phenomenon probably is responsible for the noise level for aerosols of soluble phosphorus samples and the roughly constant relative standard deviation for such measurements. For a constant relative error, a logarithmic output would provide more practical (and equally accurate) means of covering the analytical range than the range-switching technique used with linear output in the present model.

Several safety features should be incorporated in any future development of the instrument. At present, excess hydrogen from the burner is exhausted to the room. Although the flow of hydrogen is not large, it might be well to provide an afterburner to dispose of the excess.

With the use of hydrogen fuel, some sort of fail-safe device should be provided in case of flame-outs. In the original prototype, a thermocouple flame sensor activated an igniter when the flame went out, but operation was not always reliable. The thermocouple sensor might better be used to activate a solenoid shut-off valve in the hydrogen supply line. Alternatively, hydrogen might be generated electrolytically under the control of the flame sensor.

A major reason for the poorer sensitivity of the present model, as compared to the earlier prototype, is certainly due to modification of the sample aerosol introduction. In the present model all the aerosol is fed to the burner and this results in less sample reaching the flame than when a large excess of aerosol was directed against the face of the instrument in the original design. The modification was made to prevent dispersion of pathogens to the area around the instrument when,

for example, raw sewage samples are analyzed. The sample aerosolizing apparatus is still physically independent of the burner, and therefore, not foolproof. It should preferably be built into the instrument so that all aerosol is completely confined or sterilized in the flame.

SECTION VI

REFERENCES

1. Prager, M.J. "Automated Water Monitoring Instrument for Phosphorus Contents." Environmental Protection Agency, Washington, DC. Report EPA-R4-73-026. June, 1973. 25 p.

2. Seitz, W.R. "Evaluation of Flame Emission Determination of Phosphorus in Water." Environmental Protection Agency, Corvallis, OR. Report EPA-660/2-73-007. August, 1973. 18 p.

3. Kim, C.H. "Automated Water Monitoring Instrument for Phosphorus Contents." NUCOR Corporation, Denville, NJ. Unpublished. Final Report on Contract No. 68-03-0236.

4. Perry, R.H., C.H. Chilton, and S.D. Kirkpatrick, eds. Chemical Engineers' Handbook. Fourth edition. New York, McGraw-Hill Book Co., 1963. p. 5-13.

5. Syty, A. Determination of Phosphorus in Phosphate Rock by Cool Flame Emission Spectrometry. At. Absorption Newsletter 12:1-2, January-February, 1973.

6. Dagnall, R.M., K.C. Thompson, and T.S. West. Molecular-Emission Spectroscopy in Cool Flames. Analyst (London) 93:72-78, February 1968.